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(54) Title: COMPOSITIONS AND COMPOSITES OF CELLULOSIC AND LIGNOCELLULOSIC MATERIALS AND RESINS,
AND METHODS OF MAKING THE SAME

(57) Abstract: Cellulosic or lignocellulosic materials, and compositions and composites made therefrom, are disclosed.



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Compositions and Composites of Cellulosic and Lignocellulosic Materials and Resins, and Methods of Making the Same

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application is a continuation-in-part of U.S. Patent Application Serial No. 10/336,972, filed January 6, 2003, which is a continuation-in-part of U.S. Patent Application Serial No. 10/104,414, filed March 21, 2002, which is a continuation-in-part of U.S. Patent Application Serial No. 09/772,593, filed January 30, 2001, which is: (a) a continuation-in-part of U.S. Patent Application Serial No. 09/337,580, filed
10 June 22, 1999, now issued as U.S. Patent No. 6,207,729, which is a continuation in part of U.S. Patent Application No. 08/961,863, filed October 31, 1997, now issued as U.S. Patent No. 5,973,035, (b) a continuation-in-part of U.S. Patent Application Serial No. 09/338,209, filed June 22, 1999, which is a continuation-in-part of U.S. Patent Application No. 08/921,807, filed September 2, 1997, now issued as U.S. Patent No.
15 5,952,105, and (c) a continuation in part of U.S. Patent Application Serial No. 09/290,031, filed April 9, 1999, now issued as U.S. Patent No. 6,258,876, which is a division of U.S. Patent Application No. 08/961,863, filed October 31, 1997, now issued as U.S. Patent No. 5,973,035; and (2) a continuation-in-part of U.S. Patent Application Serial No. 09/593,627, filed June 13, 2000, which is a continuation-in-
20 part of U.S. Patent Application Serial Nos. 09/337,580 and 09/338,209. All of the above applications and patents are incorporated by reference in their entireties.

BACKGROUND OF THE INVENTION

The invention relates to texturized cellulosic or lignocellulosic materials and compositions and composites made from such texturized materials.

25 Cellulosic and lignocellulosic materials are produced, processed, and used in large quantities in a number of applications. Once used, these materials are usually discarded. As a result, there is an ever-increasing amount of waste cellulosic and lignocellulosic material.

SUMMARY OF THE INVENTION

In general, the invention features texturized cellulosic or lignocellulosic materials and compositions and composites made therefrom.

In one embodiment, the features a process for manufacturing a composite.

5 The method includes the steps of (a) shearing cellulosic or lignocellulosic fiber to the extent that its internal fibers are substantially exposed to form texturized cellulosic or lignocellulosic fiber, and (b) combining the cellulosic or lignocellulosic fiber with a resin. These steps can be carried out in any order (i.e., (a) then (b), or (b) then (a)) or concurrently (i.e., at around the same time). The resin can be, for example, a
10 thermoplastic resin, a thermosetting resin, an elastomer, a tar, an asphalt, or a lignin. Specific examples include polystyrene, polycarbonate, polybutylene, thermoplastic polyester, polyether, thermoplastic polyurethane, PVC, Nylon, alkyd, diallyl phthalate, epoxy, melamine, phenolic, silicone, urea, thermosetting polyester, natural rubber, isoprene rubber, styrene-butadiene copolymers, neoprene, nitrile rubber, butyl
15 rubber, ethylene propylene copolymer (i.e., "EPM"), ethylene propylene diene terpolymer (i.e., "EPDM"), hypalon, acrylic rubber, polysulfide rubber, silicones, urethanes, fluoroelastomers, butadiene, or epichlorohydrin rubber.

The fiber can be, for example, jute, kenaf, flax, hemp, cotton, rag, paper, paper products, or byproducts of paper manufacturing. Specific examples include pulp
20 board, newsprint, magazine paper, poly-coated paper, and bleached kraft board. The fiber can be a natural or synthetic cellulosic or lignocellulosic material, and can be woven or non-woven material.

The shearing step can be carried out using a rotary cutter or other mechanical method prior to combining with resin, or can be carried out *in situ* in a compounding
25 machine or extruder. In some cases, a screw in the compounding machine or extruder can be effective for shearing the material.

In certain embodiments, the method can also include, after step (a) but prior to step (b), densifying the texturized fiber. The densification step increases the bulk density of the texturized material, generally by a factor of at least two or three. In
30 some cases, the bulk density can be increased by a factor of five to ten or more. A

preferred range of bulk densities for the densified texturized fiber is about 5-25 pounds per cubic foot. A more preferred range is about 8-15 pounds per cubic foot. The densification step can result in the compression of the texturized fiber into pellets of any shape or size.

5 The composite manufactured by the above methods is also an aspect of the invention. In a typical composite of the invention, at least about 50% of the fibers have a length/diameter ratio of at least about 5 (e.g., 5, 10, 15, 25, 30, 35, 40, 50, or more)

10 A composition that includes such composites, together with a chemical or chemical formulation, is also an aspect of the invention. Examples of such chemical formulations include compatibilizers such as FUSABOND® that allow for blending, bonding, adhesion, interphasing, and/or interfacing between otherwise incompatible materials such as hydrophilic fibers and hydrophobic resins.

15 In another embodiment, the invention features a process for preparing a texturized fibrous material. The process involves shearing a cellulosic or lignocellulosic material having internal fibers (e.g., flax; hemp; cotton; jute; rags; finished or unfinished paper, paper products, including poly-coated paper, or byproducts of paper manufacturing such as pulp board; or synthetic cellulosic or lignocellulosic materials such as rayon), to the extent that the internal fibers are
20 substantially exposed, resulting in texturized fibrous material. The cellulosic or lignocellulosic material can be a woven material such as a woven fabric, or a non-woven material such as paper or bathroom tissue. The exposed fibers of the texturized fibrous material can have a length/diameter (L/D) ratio of at least about 5 (at least about 5, 10, 25, 50, or more). For example, at least about 50% of the fibers
25 can have L/D ratios of this magnitude.

 In another embodiment, the invention features a texturized fibrous material that includes a cellulosic or lignocellulosic material having internal fibers, where the cellulosic or lignocellulosic material is sheared to the extent that the internal fibers are substantially exposed.

The texturized fibrous material can, for example, be incorporated into (e.g., associated with, blended with, adjacent to, surrounded by, or within) a structure or carrier (e.g., a netting, a membrane, a flotation device, a bag, a shell, or a biodegradable substance). Optionally, the structure or carrier may itself be made from
5 a texturized fibrous material (e.g., a texturized fibrous material of the invention), or of a composition or composite of a texturized fibrous material.

The texturized fibrous material can have a bulk density less than about 0.5 grams per cubic centimeter, or even less than about 0.2 g/cm³.

Compositions that include the texturized fibrous materials described above,
10 together with a chemical or chemical formulation (e.g., a pharmaceutical such as an antibiotic or contraceptive, optionally with an excipient; an agricultural compound such as a fertilizer, herbicide, or pesticide; or a formulation that includes enzymes) are also within the scope of the invention, as are compositions that include the texturized fibrous materials and other liquid or solid ingredients (e.g., particulate, powdered, or
15 granulated solids such as plant seed, foodstuffs, or bacteria).

Composites that include thermoplastic resin and the texturized fibrous materials are also contemplated. The resin can be, for example, polyethylene, polypropylene, polystyrene, polycarbonate, polybutylene, a thermoplastic polyester, a polyether, a thermoplastic polyurethane, polyvinylchloride, or a polyamide, or a
20 combination of two or more resins.

In some cases, at least about 5% by weight (e.g., 5%, 10%, 25%, 50%, 75%, 90%, 95%, 99%, or about 100%) of the fibrous material included in the composites is texturized.

The composite may include, for example, about 30% to about 70% by weight
25 resin and about 30% to about 70% by weight texturized fibrous material, although proportions outside of these ranges may also be used. The composites can be quite strong, in some cases having a flexural strength of at least about 6,000 to 10,000 psi.

In another embodiment, the invention features a composite including a resin, such as a thermoplastic resin, and at least about 2% by weight, more preferably at
30 least about 5% by weight, texturized cellulosic or lignocellulosic fiber. The invention

also features a composite that includes polyethylene and at least about 50% by weight texturized cellulosic or lignocellulosic fiber.

The invention further features composites, including a resin and cellulosic or lignocellulosic fiber, that have flexural strengths of at least about 3,000 psi, or tensile
5 strengths of at least about 3,000 psi.

In addition, the invention features a process for manufacturing a composite; the process includes shearing cellulosic or lignocellulosic fiber to form texturized cellulosic or lignocellulosic fiber, then combining the texturized fiber with a resin. A preferred method includes shearing the fiber with a rotary knife cutter. The invention
10 also features a process for manufacturing a composite that includes shearing cellulosic or lignocellulosic fiber and combining the fiber with a resin.

The invention also features a process that includes shearing cellulosic or lignocellulosic fiber to the extent that its internal fibers are substantially exposed to form texturized cellulosic or lignocellulosic fibers, and densifying the texturized
15 cellulosic or lignocellulosic fiber. The texturized cellulosic or lignocellulosic fibers can be treated or otherwise combined with other substances before or after densification. The texturized cellulosic or lignocellulosic fibers may be, for example, treated with a substance that aids in densification and/or subsequent reopening of the densified fibers.

20 The invention also features the densified texturized cellulosic or lignocellulosic fibers.

The composites described above can also include inorganic additives such as calcium carbonate, graphite, asbestos, wollastonite, mica, glass, fiber glass, chalk, talc, silica, ceramic, ground construction waste, tire rubber powder, carbon fibers, or
25 metal fibers (e.g., stainless steel or aluminum). Such inorganic additives can represent, for example, about 0.5% to about 20% of the total weight of the composite.

The composites can be in the form of, for example, a pallet (e.g., an injection molded pallet), pipes, panels, decking materials, boards, housings, sheets, poles, straps, fencing, members, doors, shutters, awnings, shades, signs, frames, window
30 casings, backboards, wallboards, flooring, tiles, railroad ties, forms, trays, tool

handles, stalls, bedding, dispensers, staves, films, wraps, totes, barrels, boxes, packing materials, baskets, straps, slips, racks, casings, binders, dividers, walls, indoor and outdoor carpets, rugs, wovens, and mats, frames, bookcases, sculptures, chairs, tables, desks, art, toys, games, wharves, piers, boats, masts, pollution control products, septic tanks, automotive panels, substrates, computer housings, above- and below-ground electrical casings, furniture, picnic tables, tents, playgrounds, benches, shelters, sporting goods, beds, bedpans, thread, filament, cloth, plaques, trays, hangers, servers, pools, insulation, caskets, book covers, clothes, canes, crutches, and other construction, agricultural, material handling, transportation, automotive, industrial, environmental, naval, electrical, electronic, recreational, medical, textile, and consumer products. The composites can also be in the form of a fiber, filament, or film.

The terms "texturized cellulosic or lignocellulosic material" and "texturized fibrous material" as used herein, mean that the cellulosic or lignocellulosic material has been sheared to the extent that its internal fibers are substantially exposed. At least about 50%, more preferably at least about 70%, of these fibers have a length/diameter (L/D) ratio of at least 5, more preferably at least 25, or at least 50. An example of texturized cellulosic material is shown in Fig. 1.

The texturized fibrous materials of the invention have properties that render them useful for various applications. For example, the texturized fibrous materials have absorbent properties, which can be exploited, for example, for pollution control. The fibers are generally biodegradable, making them suitable, for example, for drug or chemical delivery (e.g., in the treatment of humans, animals, or in agricultural applications). The texturized fibrous materials can also be used to reinforce polymeric resins.

The term "thermosetting resin", as used herein, refers to plastics (e.g., organic polymers) that are cured, set, or hardened into a permanent shape. Curing is an irreversible chemical reaction typically involving molecular cross-linking using heat or irradiation (e.g., UV irradiation). Curing of thermosetting materials can be initiated or completed at, for example, ambient or higher temperatures. The cross-linking that

occurs in the curing reaction is brought about by the linking of atoms between or across two linear polymers, resulting in a three-dimensional rigidified chemical structure.

Examples of thermosetting resins include, but are not limited to, silicones, alkyds, diallyl phthalates (allyls), epoxies, melamines, phenolics, certain polyesters, silicones, ureas, polyurethanes, polyolefin-based thermosetting resins such as TELENET™ (BF Goodrich) and METTON™ (Hercules).

The term "elastomer", as used herein, refers to macromolecular materials that rapidly return to approximate their initial dimensions and shape after deformation and subsequent release.

Examples of elastomers include, but are not limited to, natural rubber, isoprene rubber, styrene-butadiene copolymers, neoprene, nitrile rubber, butyl rubber, ethylene propylene copolymer (i.e., "EPM") and ethylene propylene diene terpolymer (i.e., "EPDM"), hypalon, acrylic rubber, polysulfide rubber, silicones, urethanes, fluoroelastomers, butadiene, and epichlorohydrin rubber.

The term "tar", as used herein, means a typically thick brown to black liquid mixture of hydrocarbons and their derivatives obtained by distilling wood, peat, coal, shale, or other vegetable or mineral materials. An example is coal tar, which is made by destructive distillation of bituminous coal or crude petroleum (e.g., containing naphthalene, toluene, quinoline, aniline, and cresols).

The term "lignin", as used herein, refers to an amorphous substance, mixture, or powder isolated from wood, plants, recycled wood or plant products, or as a byproduct of papermaking. In nature, lignins, together with cellulose, form the woody cell walls of plants and the cementing material between them. They are typically polymeric and may be distinguished from cellulose by (1) a higher carbon content than cellulose, and (2) the inclusion of propyl-benzene units, methoxyl groups, and/or hydroxyl groups. They are generally not hydrolyzed by acids but may be soluble in hot alkali and bisulfite, and may be readily oxidizable. Lignins can be recovered from the liquor that results from the sulfate or soda process of making

cellulosic pulp, or from sulfite liquor. The term lignin thus includes sulfite lignin, or lignin-sulfonates.

The term "asphalt", as used herein, refers, for example, to an amorphous, solid, or semisolid mixture of hydrocarbons, brownish-black pitch, or bitumen, produced from the higher-boiling point minerals oils by the action of oxygen. Asphalts include both asphaltenes and carbenes. Asphalts are commonly used for paving, roofing, and waterproofing materials.

The new compositions have properties that render them useful for various applications. Compositions that include texturized fibrous material and matrices are, for example, strong, lightweight, and inexpensive.

Other advantages afforded by the texturized fibers include:

(1) Reduced densities of matrix materials such as elastomers and thermosetting resins.

(2) Higher impact resistance due to increased interfacial area between matrix and texturized fiber and increased energy absorbed when texturized fiber delaminates from matrices.

(3) Reduced surface friction.

(4) Higher lubricity surfaces.

(5) Enhanced tolerance for and compatibilization of both the hydrophobic and hydrophilic constituents in the matrices.

(6) Enhanced ability to custom tailor the properties of the composition for specific requirements.

The raw materials used to make the composites are available as virgin or recycled materials; for example, they may include discarded containers composed of resins, and waste cellulosic or lignocellulosic fiber.

Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a photograph of a texturized newspaper, magnified fifty times;

FIG. 2 is a photograph of texturized poly-coated paper, magnified fifty times;

FIG. 3 is a photograph of a half-gallon polyboard juice carton;

5 FIG. 4 is a photograph of shredded half-gallon polyboard juice cartons; and

FIG. 5 is a photograph of texturized fibrous material prepared by shearing the shredded half-gallon polyboard juice cartons of FIG. 4.

DETAILED DESCRIPTION OF THE INVENTION

10 Examples of cellulosic raw materials include paper and paper products such as newsprint, poly-coated paper, and effluent from paper manufacture; examples of lignocellulosic raw materials include wood, wood fibers, and wood-related materials, as well as materials derived from kenaf, grasses, rice hulls, bagasse, cotton, jute, other stem plants (e.g., hemp, flax, bamboo; both bast and core fibers), leaf plants (e.g.,
15 sisal, abaca), and agricultural fibers (e.g., cereal straw, corn cobs, rice hulls, and coconut hair). Aside from virgin raw materials, post-consumer, industrial (e.g., offal), and processing waste (e.g., effluent) can also be used as fiber sources.

Preparation of Texturized Fibrous Material

If scrap cellulosic or lignocellulosic materials are used, they should preferably be clean and dry, although the materials can alternatively be sheared after wetting, either with water, a solvent, a compatibilizer, or a resin. The raw material can be
5 texturized using any one of a number of mechanical means, or combinations thereof. One method of texturizing includes first cutting the cellulosic or lignocellulosic material into 1/4- to 1/2-inch pieces, if necessary, using a standard cutting apparatus. Counter-rotating screw shredders and segmented rotating screw shredders such as those manufactured by Munson (Utica, NY) can also be used, as can a standard
10 document shredder as found in many offices.

The cellulosic or lignocellulosic material can then be sheared with a rotary cutter, such as the one manufactured by Sprout, Waldron Companies, as described in Perry's Chem. Eng. Handbook, 6th Ed., at 8-29 (1984). Although other settings can be used, the spacing between the rotating knives and bed knives of the rotary cutter is
15 typically set to 0.020" or less, and blade rotation is set to 750 rpm or more. The rotary cutter can be cooled to 100°C or lower during the process, for example, using a water jacket.

The texturized material is passed through a discharge screen. Larger screens (e.g., up to 6 mm) can be used in large-scale production. The cellulosic or
20 lignocellulosic feedstock is generally kept in contact with the blades of the rotary cutter until the fibers are pulled apart; smaller screens (e.g., 2 mm mesh) provide longer residence times and more complete texturization, but can result in lower length/diameter (L/D) aspect ratios. A vacuum drawer can be attached to the screen to maximize and maintain fiber length/diameter aspect ratio.

25 The texturized fibrous materials can be directly stored in sealed bags or may be dried at approximately 105°C for 4-18 hours (e.g., until the moisture content is less than about 0.5%) immediately before use. Fig. 1 is an SEM photograph of texturized newspaper.

Alternative texturizing methods include stone grinding, mechanical ripping or
30 tearing, and other methods whereby the material's internal fibers can be exposed (e.g.,

pin grinding, air attrition milling). Examples of such other methods can also include *in situ* shearing in a compounding machine used to mix the fibers with resin or in an extruder. The fibrous material can be, for example, added before, after, or concurrent with the addition of the resin, irrespective of whether the resin is in a solid form (e.g., powdered or pelletized) form or a liquid form (e.g., molten or in solution).

After the material has been texturized, it can optionally be "densified," or compacted, to facilitate transport, storage, handling, processing, and/or feeding into compounding or extruding equipment. Densification can be carried out using a roll mill (which can form pellets or other shapes), for example, or a pellet mill.

Pelletizing machines used in agriculture, pharmaceuticals (e.g., "pilling" machines), metallurgy, and other industries can be used or adapted for use for densifying texturized fiber. Pellet mills are available from, for example, California Pellet Mill (Model Lab Mill).

During densification, the bulk density of the texturized material is increased.

For example, whereas virgin poly-coated paper might have a bulk density of, for example, 60 to 90 pounds per cubic foot, and texturized poly-coated paper might have a bulk density of about 2-6 pounds per cubic foot (i.e., about 0.03-0.1 g/cc), the densified material derived therefrom can have a bulk density, for example, of from 10 to 50 pounds per cubic foot, or from 15 to 35 pounds per cubic foot, or from 20 to 30 pounds per cubic foot, for example, 25 pounds per cubic foot. Preferably, the bulk density of the densified fiber does not exceed the bulk density of the starting **untextured** material. A bulk density in the above ranges can allow for a relatively high feed rate in an extrusion process (i.e., about 10 times greater than that of a material having a bulk density of 2.8) without destroying the integrity of the texturized fiber. The densified texturized fiber can be substituted for non-densified texturized fiber in many applications, because, even though the densified texturized fiber has a relatively high bulk density, once the densified fiber is fed into compounding, extrusion, or other processing devices, the fibers can readily re-"open" to re-expose the fibers.

Optionally, prior to densification substances can be added to the texturized material that aid in densification. Examples of substances include anti-static agents, wetting agents, stiffening agents, compatibilizers, processing aids, stabilizers, and binders. In addition, substances also can be added that aid in the reopening of the densified material; these substances can be added to the texturized material before densification or can be added directly to the densified material.

Uses of Texturized Fibrous Material

Texturized fibrous materials and compositions and composites of such fibers with other chemicals and chemical formulations can be prepared to take advantage of the materials' properties. The materials can be used to absorb chemicals, for example, potentially absorbing many times their own weight. The texturized fibrous materials can be used in these applications in either their undensified or densified form. Thus, the materials could, for instance, be used to absorb spilled oil, or for clean up of environmental pollution, for example, in water, in the air, or on land. Similarly, the material's absorbent properties, together with its biodegradability, also make them useful for delivery of chemicals or chemical formulations. For example, the materials can be treated with solutions of enzymes or pharmaceuticals such as antibiotics, nutrients, or contraceptives, and any necessary excipients, for drug delivery (e.g., for treatment of humans or animals, or for use as or in animal feed and/or bedding), as well as with solutions of fertilizers, herbicides, or pesticides. The materials can optionally be chemically treated to enhance a specific absorption property. For example, the materials can be treated with silanes to render them lipophilic. The texturized fibrous materials optionally can be combined with the chemicals or chemical formulations or otherwise treated, and then densified. In addition, densified texturized fibrous material optionally can be combined with the chemicals or chemical formulations or otherwise treated.

Compositions including texturized materials combined with liquids or particulate, powdered, or granulated solids can also be prepared. For example, texturized materials can be blended with seeds (i.e., with or without treatment with a solution of fertilizer, pesticides, etc.), foodstuffs, or bacteria (e.g., bacteria that digest

toxins). The ratio of fibrous materials to the other components of the compositions will depend on the nature of the components and readily be adjusted for a specific product application. Optionally, the texturized material can be combined with the other component(s), and the combination densified. In addition, the texturized material can be combined with the other component(s) after densification.

In some cases, it may be advantageous to associate the texturized fibrous materials, or compositions or composites of such materials, with a structure or carrier such as a netting, a membrane, a flotation device, a bag, a shell, or a biodegradable substance. Optionally, the structure of carrier may itself be made of a texturized fibrous material (e.g., a material of the invention), or a composition or composite thereof.

Composites of Texturized Fibrous Material and Resin

Texturized fibrous materials, optionally in densified form, can also be combined with resins to form strong, lightweight composites. Materials that have been treated with chemicals or chemical formulations, as described above, can similarly be combined with biodegradable or non-biodegradable resins to form composites, allowing the introduction of, for example, hydrophilic substances into otherwise hydrophobic polymer matrices. Alternatively, the composites including texturized fibrous materials and resin can be treated with chemicals or chemical formulations.

The texturized cellulosic or lignocellulosic material provides the composite with strength. The composite may include from about 10% to about 90%, for example from about 30% to about 70%, of the texturized cellulosic or lignocellulosic material by weight.

The resin encapsulates the texturized cellulosic or lignocellulosic material in the composites, and helps control the shape of the composites. The resin also transfers external loads to the fibrous materials and protects the fiber from environmental and structural damage. Composites can include, for example, about 10% to about 90%, more preferably about 30% to about 70%, by weight, of the resin.

Resins are used in a variety of applications, for example, in food packaging. Food containers made of resins are typically used once, and then discarded. Examples of resins that are suitably combined with texturized fibers include polyethylene (including, e.g., low density polyethylene and high density
5 polyethylene), polypropylene, polystyrene, polycarbonate, polybutylene, thermoplastic polyesters (e.g., PET), polyethers, thermoplastic polyurethane, PVC, polyamides (e.g., nylon) and other resins. It is preferred that the resins have a low melt flow index. Preferred resins include polyethylene and polypropylene with melt flow indices of less than 3 g/10 min, and more preferably less than 1 g/10 min.

10 The resins can be purchased as virgin material, or obtained as waste materials, and can be purchased in pelletized or granulated form. One source of waste resin is used polyethylene milk bottles. If surface moisture is present on the pelletized or granulated resin, however, it should be dried before use.

The composites can also include coupling agents. The coupling agents help to
15 bond the hydrophilic fibers to the hydrophobic resins. Examples of coupling agents include maleic anhydride modified polyethylenes, such as those in the FUSABOND® (available from Dupont, Delaware) and POLYBOND® (available from Uniroyal Chemical, Connecticut) series. One suitable coupling agent is a maleic anhydride modified high-density polyethylene such as FUSABOND® MB 100D.

20 The composites can also contain additives known to those in the art of compounding, such as plasticizers, lubricants, antioxidants, opacifiers, heat stabilizers, colorants, flame-retardants, biocides, impact modifiers, photostabilizers, and antistatic agents.

The composites can also include inorganic additives such as calcium
25 carbonate, graphite, asbestos, wollastonite, mica, glass, fiber glass, chalk, silica, talc, ceramic, ground construction waste, tire rubber powder, carbon fibers, or metal fibers (e.g., aluminum, stainless steel). When such additives are included, they are typically present in quantities of from about 0.5% up to about 20-30% by weight. For example, submicron calcium carbonate can be added to the composites of fiber and resin to
30 improve impact modification characteristics or to enhance composite strength.

The resin, coupling agent, and other additives discussed above can be combined with the texturized material, and resultant compositions optionally can be densified.

Preparation of Compositions

5 Compositions containing the texturized cellulosic or lignocellulosic materials and chemicals, chemical formulations, or other solids can be prepared, for example, in various immersion, spraying, or blending apparatuses, including, but not limited to, ribbon blenders, cone blenders, double cone blenders, and Patterson-Kelly "V" blenders.

10 For example, a composition containing 90% by weight texturized cellulosic or lignocellulosic material and 10% by weight ammonium phosphate or sodium bicarbonate can be prepared in a cone blender to create a fire-retardant material for absorbing oil.

Preparation of Composites of Texturized Fiber and Resin

15 Composites of texturized fibrous material and resin can be prepared as follows. A standard rubber/plastic compounding 2-roll mill is heated to 325-400°F. The resin (usually in the form of pellets or granules) is added to the heated roll mill. After about 5 to 10 minutes, the coupling agent is added to the roll mill. After another five minutes, the texturized cellulosic or lignocellulosic material is added to the
20 molten resin/coupling agent mixture. The texturized material is added over a period of about 10 minutes.

The composite is removed from the roll mill, cut into sheets and allowed to cool to room temperature. It is then compression molded into plaques using standard compression molding techniques:

25 Alternatively, a mixer, such as a Banbury internal mixer, is charged with the ingredients. The ingredients are mixed, while the temperature is preferably maintained at less than about 190°C. The mixture can then be compression molded.

In another embodiment, the ingredients can be mixed in an extruder mixer, such as a twin-screw extruder equipped with co-rotating screws. The resin and the

coupling agent are introduced at the extruder feed throat; the texturized cellulosic or lignocellulosic material is introduced about 1/3 of the way down the length of the extruder into the molten resin. The internal temperature of the extruder is preferably maintained at less than about 190°C, although higher temperatures (e.g., 270°C) might be encountered during extrusion of certain profiles. At the output, the composite can be, for example, pelletized by cold strand cutting.

Alternatively, the mixture can first be prepared in a mixer, then transferred to an extruder.

In another embodiment, the composite can be formed into fibers, using fiber-forming techniques known to those in the art, or into filaments for knitting, warping, weaving, braiding, or making non-wovens. In a further embodiment, the composite can be made into a film.

Properties of the Composites of Texturized Fibrous Material and Resin

The resulting composites include a network of fibers, encapsulated within a resin matrix. The fibers form a lattice network, which provides the composite with strength. Since the cellulosic or lignocellulosic material is texturized, the amount of surface area available to bond to the resin is increased, in comparison to composites prepared with un-texturized cellulosic or lignocellulosic material. The resin binds to the surfaces of the exposed fibers, creating an intimate blend of the fiber network and the resin matrix. The intimate blending of the fibers and the resin matrix further strengthens the composites.

These compositions can also include inorganic additives such as calcium carbonate, graphite, asbestos, wollastonite, mica, glass, fiber glass, chalk, silica, talc, flame retardants such as alumina trihydrate or magnesium hydroxide, ground construction waste, tire rubber powder, carbon fibers, or metal fibers (e.g., aluminum, stainless steel). These additives may reinforce, extend, change electrical or mechanical or compatibility properties, and may provide other benefits. When such additives are included, they may be present in loadings by weight from below 1% to as high as 80%. Typical loadings ranges are between 0.5% and 50% by weight.

Polymeric and elastomeric compositions can also include coupling agents. The coupling agents help to bond the hydrophilic fibers of the texturized fibrous material to the resins.

5 The compositions having thermosetting or elastomer matrices can also contain additives known to those in the art of compounding, such as plasticizers; lubricants; antioxidants; opacifiers; heat stabilizers; colorants; impact modifiers; photostabilizers; biocides; antistatic agents; organic or inorganic flame retardants, biodegradation agents; and dispersants. Special fiber surface treatments and additives can be used when a specific formulation requires specific property improvement.

10 The following are non-limiting examples of compositions:

Thermosetting Resins: Compositions of texturized fibrous material and thermosetting resins can be prepared as bulk molding compounds (BMCs), sheet molding compounds (SMCs), or as other formulations.

15 Bulk molding compounds (BMCs) are materials made by combining a resin and chopped fibers in a dough mixer, then mixing until the fibers are well wetted and the material has the consistency of modeling clay. Most BMCs are based on polyesters, but vinyl esters and epoxies are sometimes used. A pre-weighed amount of the compound is placed in a compression mold, which is then closed and heated under pressure to cross-link the thermosetting polymer. Many electrical parts are
20 made using BMC compounds and processing. Other applications include microwave dishes, tabletops, and electrical insulator boxes.

Sheet molding compounds (SMCs) are made by compounding a polyester resin with fillers, pigments, catalysts, mold release agents, and/or special thickeners that react with the polymer to greatly increase the viscosity. The resin mixture is
25 spread onto a moving nylon film. The resin passes under feeders, which disperse the texturized fibers. A second film is placed on top, sandwiching the compound inside. The material then passes through rollers that help the resin to wet the fibers, and the material is rolled up. Prior to use, the nylon films are removed and the compound is molded.

Other techniques and preparation procedures can be used to prepare and cure thermosetting systems.

Elastomers: Compositions of texturized fibrous material and elastomers can be prepared by known methods. In one method, for example, the elastomer is added to a rubber/plastic compounding two-roll mill. After a couple of minutes, the other ingredients, including a vulcanizing agent, are added to the roll mill. Once the elastomer has been compounded, the texturized fibrous material is added to the roll mill. The texturized fibrous material is added over a period of about 10 minutes. The compounded material is removed from the roll mill and cut into sheets. It is then compression molded into the desired shape using standard compression molding techniques.

Alternatively, a mixer, such as a Banbury internal mixer or appropriate twin or single screw compounder can be used. If a Banbury mixer is used, the compounded mixture can, for example, be discharged and dropped onto a roll mill for sheeting. Single or twin-screw compounders produce a sheet as an extrudate. The mixture can then be compression molded. Likewise, single- or twin-screw compounders can extrude a shaped profile that can be directly vulcanized. The composition can be molded, extruded, compressed, cut, or milled.

Uses of the Composites of Texturized Fibrous Material and Resin

The resin/fibrous material composites can be used in a number of applications. The composites are strong and light weight; they can be used, for example, as wood substitutes. The resin coating renders the composites water-resistant, so they may be
5 used in outdoor applications. For example, the composites may be used to make pallets, which are often stored outdoors for extended periods of time, wine staves, rowboats, furniture, skis, and oars. Many other uses are contemplated, including panels, pipes, decking materials, boards, housings, sheets, poles, straps, fencing, members, doors, shutters, awnings, shades, signs, frames, window casings,
10 backboards, wallboards, flooring, tiles, railroad ties, forms, trays, tool handles, stalls, bedding, dispensers, staves, films, wraps, totes, barrels, boxes, packing materials, baskets, straps, slips, racks, casings, binders, dividers, walls, indoor and outdoor carpets, rugs, wovens, and mats, frames, bookcases, sculptures, chairs, tables, desks, art, toys, games, wharves, piers, boats, masts, pollution control products, septic tanks,
15 automotive panels, substrates, computer housings, above- and below-ground electrical casings, furniture, picnic tables, tents, playgrounds, benches, shelters, sporting goods, beds, bedpans, thread, filament, cloth, plaques, trays, hangers, servers, pools, insulation, caskets, book covers, clothes, canes, crutches, and other construction, agricultural, material handling, transportation, automotive, industrial, environmental,
20 naval, electrical, electronic, recreational, medical, textile, and consumer products. Numerous other applications are also envisioned. The composites may also be used, for example, as the base or carcass for a veneer product, or sandwiched between layers of paper or other material.. Moreover, the composites can be, for example, surface treated, grooved, milled, shaped, imprinted, textured, compressed, punched, or
25 colored.

The following examples illustrate certain embodiments and aspects of the present invention and not to be construed as limiting the scope thereof.

EXAMPLES

Example 1

A 1500-pound skid of virgin, half-gallon juice cartons made of poly-coated white kraft board was obtained from International Paper. One such carton is shown in
5 FIG. 3. Each carton was folded flat.

The cartons were fed into a 3 hp Flinch Baugh shredder at a rate of approximately 15 to 20 pounds per hour. The shredder was equipped with two rotary blades, each 12" in length, two fixed blades, and a 0.3" discharge screen. The gap between the rotary and fixed blades was 0.10".

10 A sample of the output from the shredder, consisting primarily of confetti-like pieces, about 0.1" to 0.5" in width and about 0.25" to 1" in length, is shown in FIG. 4. The shredder output was fed into a Thomas Wiley Mill Model 2D5 rotary cutter. The rotary cutter had four rotary blades, four fixed blades, and a 2 mm discharge screen. Each blade was approximately 2" long. The blade gap was set at 0.020".

15 The rotary cutter sheared the confetti-like pieces across the knife edges, tearing the pieces apart and releasing a finely texturized fiber at a rate of about one pound per hour. The fiber had an average minimum L/D ratio of between five and 100 or more. The bulk density of the texturized fiber was on the order of 0.1 g/cc. A sample of texturized fiber is shown in FIG. 5 at normal magnification, and in FIG. 2
20 at fifty-fold magnification.

Example 2

Composites of texturized fiber and resin were prepared as follows. A standard rubber/plastic compounding 2-roll mill was heated to 325-400°F. The resin (usually in the form of pellets or granules) was added to the heated roll mill. After about 5 to
25 10 minutes, the resin banded on the rolls (i.e., it melted and fused on the rolls). The coupling agent was then added to the roll mill. After another five minutes, the texturized cellulosic or lignocellulosic material was added to the molten resin/coupling agent mixture. The cellulosic or lignocellulosic fiber was added over a period of about 10 minutes.

The composite was then removed from the roll mill, cut into sheets, and allowed to cool to room temperature. Batches of about 80 g each were compression molded into 6" x 6" x 1/8" plaques using standard compression molding techniques.

One composition contained the following ingredients:

5	<u>Composition No. 1</u>	
	<u>Ingredient</u>	<u>Amount(g)</u>
	High density polyethylene ¹	160
	Old newspaper ²	240
	Coupling agent ³	8
10	¹ Marlex 16007	
	² Texturized using rotary cutter with 2 mm mesh	
	³ FUSABOND® 100D	

The plaques were machined into appropriate test specimens and tested according to the procedures outlined in the method specified. Three different specimens were tested for each property, and the mean value for each test was calculated.

The properties of Composition No. 1 are as follows:

Flexural strength (10^3 psi)	9.81 (ASTM D790)
Flexural modulus (10^5 psi)	6.27 (ASTM D790)

20

A second composition contains the following ingredients:

	<u>Composition No. 2</u>	
	<u>Ingredient</u>	<u>Amount(g)</u>
	High density polyethylene ¹	160
25	Old magazines ²	240
	Coupling agent ³	8

The properties of Composition No. 2 are as follows:

Flexural strength (10^3 psi) 9.06 (ASTM D790)

Flexural modulus (10^5 psi) 6.78 (ASTM D790)

A third composition contains the following ingredients:

5

Composition No. 3

<u>Ingredient</u>	<u>Amount(g)</u>
HDPE ¹	160
Fiber paper ²	216
3.1 mm texturized kenaf	24
Coupling agent ³	8

10

The properties of Composition No. 3 are as follows:

Flexural strength (10^3 psi) 11.4 (ASTM D790)

Flexural modulus (10^5 psi) 6.41 (ASTM D790)

A fourth composition contains the following ingredients:

15

Composition No. 4

<u>Ingredient</u>	<u>Amount (g)</u>
SUPERFLEX® CaCO ₃	33
Fiber ^{2,4}	67
HDPE (w/3% compatibilizer) ^{1,3}	100
⁴ Virgin poly-coated milk cartons	

20

The properties of Composition No. 4 are as follows:

Flexural strength (10^5 psi) 8.29 (ASTM D790)

Ultimate elongation (%) <5 (ASTM D638)

Flexural modulus (10^5 psi) 10.1 (ASTM D790)

25

Notch Izod (ft-lb/in) 1.39 (ASTM D256-97)

A fifth composition contains the following ingredients:

Composition No. 5

	<u>Ingredient</u>	<u>Amount (parts)</u>
	SUPERFLEX® CaCO ₃	22
5	Fiber ^{2,4}	67
	HDPE (w/3% compatibilizer) ^{1,3}	100

The properties of Composition No. 5 are as follows:

	Flexural strength (10 ⁵ psi)	8.38 (ASTM D790)
	Ultimate elongation (%)	<5 (ASTM D638)
10	Flexural modulus (10 ⁵ psi)	9.86 (ASTM D790)
	Notch Izod (ft-lb/in)	1.37 (ASTM D256-97)

A sixth composition contains the following ingredients:

Composition No. 6

	<u>Ingredient</u>	<u>Amount (parts)</u>
15	ULTRAFLEX® CaCO ₃	33
	Fiber ^{2,4}	67
	HDPE/compatibilizer ^{1,3}	100

The properties of Composition No. 6 are as follows:

	Flexural strength (10 ⁵ psi)	7.43 (ASTM D790)
20	Ultimate elongation (%)	<5 (ASTM D638)
	Flexural modulus (10 ⁵ psi)	11.6 (ASTM D790)
	Notch Izod (ft-lb/in)	1.27 (ASTM D256-97)

A seventh composition contains the following ingredients:

Composition No. 7

<u>Ingredient</u>	<u>Amount (pbw)</u>
HDPE (w/3% compatibilizer) ^{3,5}	60
Kraftboard ²	40
⁵ HDPE with melt-flow index	<1

The properties of Composition No. 7 are as follows:

Flexural Strength (10 ⁵ psi)	7.79 (ASTM D790)
Ultimate elongation (%)	<5 (ASTM D638)
Flexural Modulus (10 ⁵ psi)	7.19 (ASTM D790)

Example 3

Foamed epoxies are used in thermal insulation applications where superior water resistance and elevated temperature properties are desired. Such epoxies can be reinforced with texturized fiber prepared according to the procedure in Example 3.

Fillers such as calcium carbonate may optionally be used to obtain some cost

reductions. However, overloading with filler can weaken the strength of the foam cell walls, particularly when the foam densities are in the range of five pounds per cubic foot or less, since such low foam density can result in thin, fragile walls within the foam. Filler loadings are generally in the four to five pounds/hundred weight (phr) of resin. Reinforcing with texturized fiber can also provide for reduced weight and cost. In addition, improved strength can be realized because of the high length-to-diameter (L/D) ratios of the texturized fiber. It is not unreasonable to employ up to 30 phr of the fiber.

A typical formulation includes:

<u>Ingredient</u>	<u>Parts</u>
DGEBA (diglycidyl ether, of bisphenol A)	100

	MPDA (<i>m</i> -phenylenediamine)	10
	Celogen® (<i>p,p</i> -oxybis-benzenesulfonylhydrazide)	10
	(Uniroyal Chemical Company)	
	Surfactant	0.15
5	Styrene Oxide	5
	Texturized Fiber	30

This formulation is mixed using standard epoxy mixing techniques. It produces a very high exotherm at the curing temperature of 120°C and a foam density of about seven pounds per cubic foot.

10 Other embodiments are within the claims.

WHAT IS CLAIMED IS:

1. A process for manufacturing a composite comprising, in any order or concurrently, (a) shearing cellulosic or lignocellulosic fiber to the extent that its internal fibers are substantially exposed to form texturized cellulosic or
5 lignocellulosic fiber, (b) densifying the texturized fiber, and (c) combining the cellulosic or lignocellulosic fiber with a resin.
2. The process of claim 1, wherein the resin is a thermoplastic resin.
3. The process of claim 1, wherein the resin is selected from the group consisting of polystyrene, polycarbonate, polybutylene, thermoplastic polyesters,
10 polyethers, thermoplastic polyurethane, PVC, and Nylon.
4. The process of claim 1, wherein the resin is selected from the group consisting of a thermosetting resin, an elastomer, a tar, an asphalt, and a lignin.
5. The process of claim 1, wherein the resin is selected from the group consisting of alkyds, diallyl phthalates, epoxies, melamines, phenolics, silicones,
15 ureas, thermosetting polyesters, natural rubber, isoprene rubber, styrene-butadiene copolymers, neoprene, nitrile rubber, butyl rubber, ethylene propylene copolymer, ethylene propylene diene terpolymer, hypalon, acrylic rubber, polysulfide rubber, silicones, urethanes, fluoroelastomers, butadiene, and epichlorohydrin rubber.
6. The process of claim 1, wherein the fiber is selected from the group
20 consisting of jute, kenaf, flax, hemp, cotton, rags, paper, paper products, and byproducts of paper manufacturing.
7. The process of claim 6, wherein the cellulosic or lignocellulosic material is pulp board.
8. The process of claim 6, wherein the paper is selected from the group
25 consisting of newsprint, magazine paper, poly-coated paper, and bleached kraft board.
9. The process of claim 1, wherein the cellulosic or lignocellulosic material is a synthetic material.
10. The process of claim 1, wherein the cellulosic or lignocellulosic material is a non-woven material.

11. The process of claim 1, wherein the step of shearing the cellulosic or lignocellulosic fiber comprises shearing with a screw in a compounding machine or extruder.

12. The process of claim 1, wherein the composite comprises about 30% to about 70% by weight resin and about 30% to about 70% by weight fiber.

13. The process of claim 1, wherein the densifying step comprises compressing at least some of the texturized fiber into pellets.

14. A composite manufactured by the process of claim 1.

15. The composite of claim 14, wherein at least about 50% of the fibers have a length/diameter ratio of at least about 5.

16. The composite of claim 14, wherein at least about 50% of the fibers have a length/diameter ratio of at least about 25.

17. The composite of claim 14, wherein at least about 50% of the fibers have a length/diameter ratio of at least about 50.

18. A composition comprising the composite of claim 14 and a chemical or chemical formulation.

19. The composition of claim 18, wherein the chemical formulation comprises a compatibilizer.

20. The composite of claim 14, further comprising an inorganic additive.

21. The composite of claim 20, wherein the inorganic additive is selected from the group consisting of calcium carbonate, graphite, asbestos, wollastonite, mica, glass, fiber glass, chalk, talc, silica, ceramic, ground construction waste, tire rubber powder, carbon fibers, and metal fibers.

22. The composite of claim 20, wherein the inorganic additive comprises from about 0.5% to about 20% of the total weight of the composite.

23. The composite of claim 14, wherein said composite is in the form of a pallet.

24. The composite of claim 14, wherein said composite is in the form of an article selected from the group consisting of panels, pipes, decking materials, boards, housings, sheets, poles, straps, fencing, members, doors, shutters, awnings, shades, signs, frames, window casings, backboards, wallboards, flooring, tiles, railroad ties, forms, trays, tool handles, stalls, bedding, dispensers, staves, films, wraps, totes, barrels, boxes, packing materials, baskets, straps, slips, racks, casings, binders, dividers, walls, indoor and outdoor carpets, rugs, wovens, and mats, frames, bookcases, sculptures, chairs, tables, desks, art, toys, games, wharves, piers, boats, masts, pollution control products, septic tanks, automotive panels, substrates, computer housings, above- and below-ground electrical casings, furniture, picnic tables, tents, playgrounds, benches, shelters, sporting goods, beds, bedpans, thread, filament, cloth, plaques, trays, hangers, servers, pools, insulation, caskets, book covers, clothes, canes, crutches, and other construction, agricultural, material handling, transportation, automotive, industrial, environmental, naval, electrical, electronic, recreational, medical, textile, and consumer products.

25. The composite of claim 14, wherein said composite is in the form of a fiber, filament, or film.

26. A process comprising

(a) shearing cellulosic or lignocellulosic fiber to the extent that its internal fibers are substantially exposed to form texturized cellulosic or lignocellulosic fibers, and

(b) densifying the texturized cellulosic or lignocellulosic fibers.

27. The process of claim 26, wherein the densifying step comprises compressing at least some of the texturized fibers into pellets.

28. The process of claim 26, further comprising, prior to the densifying step, the texturized cellulosic or lignocellulosic fibers with a substance that aids in densification.

29. The process of claim 26, further comprising combining the texturized cellulosic or lignocellulosic fibers with a resin before the densifying step.

30. The process of claim 26, further comprising combining the texturized cellulosic or lignocellulosic fiber with another substance before densification.

31. The process of claim 30, wherein the combining step comprises the texturized cellulosic or lignocellulosic fibers with a solution of an enzyme or
5 pharmaceutical.

32. The process of claim 30, wherein the combining step comprises blending the texturized cellulosic or lignocellulosic fibers with a solid.

33. A composite manufactured by the process of claim 34.

34. Densified texturized cellulosic or lignocellulosic fibers.

10 35. The densified fibers of claim 34, wherein the densified fibers have a bulk density of from 10 to 50 pounds per cubic foot.

36. The densified fibers of claim 34, wherein the densified fibers have a bulk density of from 20 to 30 pounds per cubic foot.

37. The densified fibers of claim 34, in the form of a pellet.

15

1/3

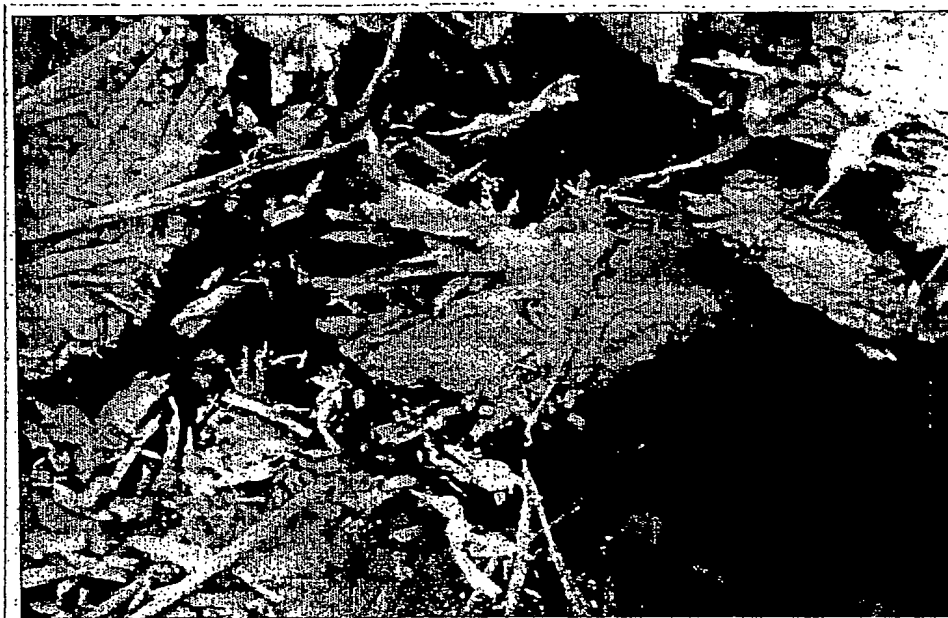


FIG. 1

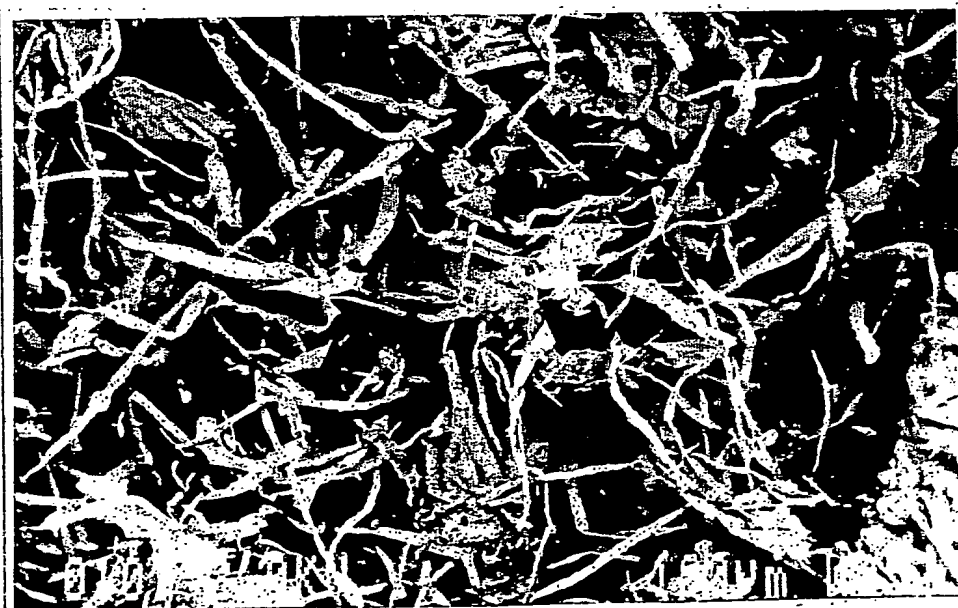


FIG. 2

2/3



FIG. 3

3/3



FIG. 4

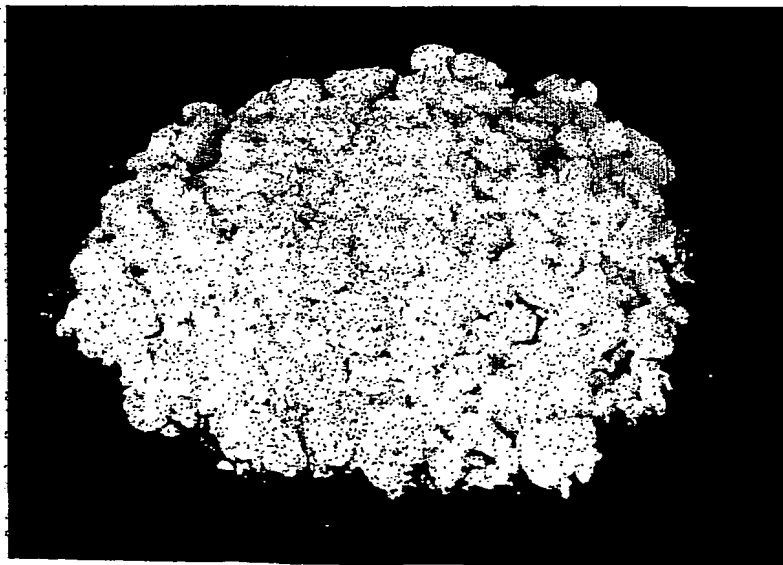


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/07765

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : A01G 9/02, 13/00; A01N 25/00, 25/34; A23G 3/00; B32B 9/04; C08J 3/00, 3/20; C09K 11/00
US CL : 524/13, 14, 76, 129; 523/129; 424/94.1, 405, 411, 413, 414; 428/364, 374, 411.1; 47/26, 65.5; 111/20
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/13, 14, 76, 129; 523/129; 424/94.1, 405, 411, 413, 414; 428/364, 374, 411.1; 47/26, 65.5; 111/20; 426/5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,973,035 A (MEDOFF et al) 26 October 1999 (26.10.1999), see claims 1-8, 11 and 14-16.	18-21
X	US 6,207,729 B1 (MEDOFF et al) 27 March 2001 (27.03.2001), see claims 9, 24, 26, 27, 31-34, 36 and 37.	18, 24-29
X	US 6,258,876 B1 (MEDOFF et al) 10 July 2001 (10.07.2001), see claims 1 and 2.	1, 2
X, P	US 6,448,307 B1 (MEDOFF et al) 10 September 2002, (10.09.2002), see claims 1, 11-13, 17-19, 21-35 and 37-48.	18-26, 28, 29

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

29 April 2003 (29.04.2003)

Date of mailing of the international search report

16 JUN 2003

Name and mailing address of the ISA/US

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Authorized officer

Nathan M. Nutter

Telephone No. 703-308-0661

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/07765

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claim Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Please See Continuation Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-25

Remark on Protest

☐
☐

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claim(s) 1-13, drawn to a process for manufacturing a composite, and the composite made.

Group II, claim(s) 14-25, drawn to a composite.

Group III, claim(s) 26-32, drawn to a process for producing texturized cellulosic fibers.

Group IV, claim(s) 34-37, drawn to texturized fibers.

The inventions listed as Groups I-V do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the Group I and Group II inventions may be grouped together as product and process of making, in accordance with 37 CFR 1.475(b)(1). The Group III claims are drawn to a process of making, but not for making either the composite of Group I or the fibers of Group IV.

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